Multidisciplinary study of glazed ceramics from Chamberí Metro Station (Madrid, Spain): A knowledge base with technological and heritage value

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A B S T R A C T

Glazed ceramics -both original and replacement- from Chamberí Metro Station (built in 1919) in Madrid (Spain) were studied using a multidisciplinary approach aimed at finding out more about the materials and technologies used to make them. The original white tiles, which help illuminate these underground spaces, were manu-factured in Onda, Castellón (Spain) with very calcareous clays fired at ≈950 °C and coated with lead alkali-glazes. The original decorative pieces, with a metallic sheen, were made in Triana, Seville (Spain) with cal-careous and illite clays fired at temperatures of between 850 and 950 °C and treated with transparent lead glazes. The replacement pieces had the same appearance as the originals but were more resistant. The white tiles were made out of quartz-rich, illite-kaolinite and calcareous clays fired at temperatures of > 950 °C with an alkali-glaze that was very rich in zircon and aluminium. The decorative pieces were made from illite-kaolinite clays very rich in aluminium and fired at < 850 °C. These included an additive in the form of a highly refractory grog and were covered with an aluminium-rich lead-potassium glaze. The manufacturing techniques used to make each type of piece varied depending on their particular function within the station.

Keywords: Spanish clayey materials Advertising tiles, Refractory clay bodies Copper metallic sheen Body-glaze interphase, Zirconia crystals

1. Introduction

1.1. Glazed ceramics technology

The study of glazed ceramics offers a fascinating insight into a craft that has skilfully combined art and technology for thousands of years. It can provide information about traditions, raw materials, production technologies and the particular skills applied (Marrocchino et al., 2010). The manufacturers must select the most appropriate materials and technologies to make the ceramic products according to the re-quired specifications, while keeping production costs as low as possible (Dondi et al., 2014). Multidisciplinary studies of traditional ceramics can help build a knowledge base of great value in technological and heritage terms. This can then be applied to ensure the successful con-servation and restoration of these ceramics, as well as to garner a better understanding of the cultures that produced them (Pérez-Monserrat et al., 2017a,b).

The most important technological characteristic of ceramic is the capacity of malleable clayey materials to harden when subjected to high temperatures (Peters and Iberg, 1978; Heimann, 1989). These materials are very versatile, a quality that can be enhanced by mixing together different clayey raw materials or by using additives which improve their properties (Kingery and Vandiever, 1986; Rice, 1987). Various mineral and textural transformations take place during firing. The crystalline structures decompose once their thermal stability limit has been reached, creating new mineral phases which can coexist alongside the original phases (Jordán et al., 1999; Maritan et al., 2006; Rathossi and Pontikes, 2010; Pardo et al., 2011).

Ceramic materials can be used either raw or covered with glaze. The layer of glaze is highly adherent to the clay body and acts as a binding agent, in addition to providing a protective and decorative coating (Kingery and Vandiever, 1986). Tite et al. (1998) noted that the first glazes were used in the Near East and Egypt around 1500 BCE and were strongly alkaline. In the Western world, lead glazes began to be used around the first century BCE. In Lower Mesopotamia glazed bricks were first used for cladding buildings around 2000 BCE and became very

popular in the Ancient City of Babylon at the height of its power (around the 7th century BCE). Of all the opacifying oxides, tin oxide is the one that behaves best over a wide range of temperatures. However, due to its high cost and toxicity it has gradually been replaced by ti-tanium, zirconium and zinc oxides (Tite et al., 1998; Karasu et al., 2000). One decorative feature achieved with glazed ceramics is the metallic sheen, a technique involving the saturation of copper. During firing (at around 1000 °C), the piece is first subjected to an oxidising phase and then to a reducing phase (Matthes, 1990; Fernández-Navarro, 2003). Lead glazes typically melt at temperatures of between 700 and 1000 °C, depending on the composition of the glaze (Geller and Bunting, 1936). During firing, elements of the clay are diffused from the body to the glaze, while lead from the glaze is diffused to the body. This encourages the nucleation of crystals, generally lead-rich feldspar, in the glaze/clay body contact zone -known as the interphase- (Molera et al., 2001; Casasola et al., 2012). The formation of these crystals, their amount and size provide clues about the procedures used to make the glaze (Molera et al., 2001). The thickness of the interphase may also indicate whether the pieces were made by single or double firing. Greater thickness indicates the former (Coll Conesa, 2014).

1.2. The use of glazed ceramics in early 20th century architecture in Madrid: The Metro Stations

Tiles have enjoyed great prestige in Spain throughout history, lar-gely due to the cultural legacy bequeathed by the Muslims. They be-came popular as an impermeable material easy to clean. Over time their use has extended to other areas and with an essentially decorative function. In Madrid, the use of glazed ceramics in architecture reached its peak in the late 19th and early 20th centuries. At that time, tiles became popular in advertising, especially in the Metro stations (Perla, 2001).

Previous analysis of original and replacement glazed ceramics used in Madrilenian buildings at the beginning of the 20th century (Pérez-Monserrat et al., 2013) makes clear: i) their essential role in the ideology of the projects, ii) the conscious decision to select Spanish raw materials, and iii) when making the replacement pieces, the appearance of the originals were respected, while using raw materials and tech-nology that made them more resistant.

By the beginning of the 20th century the population of Madrid had reached such a high level that in 1913 the engineers Carlos Mendoza (1872–1950), Miguel Otamendi (1878–1958) and Antonio González (1864–1942) presented a project for a Metro train network. The ar-chitect Antonio Palacios (1874–1945) was responsible for designing the stations, accesses and other buildings. The idea was to use traditional materials within a completely new technological environment (Olivares Abengozar, 2015). The first Metro line was inaugurated by King Alfonso XIII in 1919. It had six stations, one of which was Chamberí. Glazed ceramics made with Spanish raw materials (Fig. 1a) were used to decorate the stations as a way of brightening up or illuminating these new spaces for people who were used to natural light, "*for which purpose the rich variety of ceramics from the different Spanish regions were perfectly suited*" (Otamendi, 1919). Chamberí station was closed in 1966 and the advertising panels were covered up with cloth and paper, so protecting the tiles for several decades. In 2008, after considerable cleaning, conservation and restoration work the station was reopened to the public as the Museum of the Metro of Madrid (Figs. 1b–e).

1.3. Background information about the raw materials and technologies used in the manufacture of the glazed ceramics in Chamberí Metro Station (original and replacement pieces)

Originally, the walls and ceilings were covered with white tiles (Figs. 1b–e) made in Onda (Castellón, Spain) and the advertising panels were framed by decorative pieces (relief-tiles and ropework pieces) made in Triana (Seville, Spain) (Perla, 2001).

In the second half of the 19th century, most of the new tile factories in Spain were set up in the province of Castellón. The tertiary clays from the Miocene quarried in the nearby claypit at Sitjar (Onda) have a yellowish tone and a very high carbonate content. In order to ensure the required compactness of the ceramic pieces, these clays were mixed above all with the permo-triassic clays from Saint Joan de Moró, also in Castellón (Sanfeliu et al., 1989; Sanfeliú, 1991; Jordán et al., 2009). These clays, generically referred to as Moro clay, are rich in quartz -due to their proximity to the paleozoic metamorphic basement- and have a low carbonate content (Alonso-Azcárate et al., 1997; Jordán et al., 1999, 2009). The clays traditionally used in the ceramics industry in Seville, in which Triana was the main production centre, were Tertiary illitic calcareous clays from the banks of the River Guadalquivir, with sandy materials from the quaternary alluvium (González-García and García Ramos, 1966, González-García et al., 1988, 1990; Flores et al., 1999; Leguey et al., 2001; Rincón et al., 2008). There is documentary evidence of single firing of lead glazes in later stages of Al-Andalus, while double firing was predominant in the Caliphate and Taifa periods (Coll Conesa, 2014). Single firing was incorporated systematically into industrial tile-making production processes from the 1960s and 70s onwards (Escardino, 1992).

In the restoration work carried out in the Chamberí station in 2007–2008, all the pieces were cleaned and some were repaired. Due to leaks in some areas of the vaulted ceilings, several old pieces had to be replaced by new ones with a similar appearance to the original. The replacement pieces were made by Óscar Arribas (Decoraciones Cerámicas Madrileñas S.L.) and the industrial ceramic pastes by Cerámicas Collet S.A. (Esparreguera, Barcelona, Spain). Most of the raw materials were Spanish (Fig. 1a), in particular two of the products sold under the SIO-2® brand: the terracotta paste (PT) for the white tiles and the "lila" refractory paste (PRL) for the ropework pieces. PT is made with a mixture of illitic-calcareous clays from El Papiol (Barcelona) and Castellón, while PRL is made out of a mixture of iron-rich clays from Alcañiz (Teruel) with the important addition of an aluminium-rich grog calcined at about 1400 °C. Both ceramic pastes were pressed before the application of the glazes. An industrial tiling method was used for the glaze on the white tiles which was mechanically sprinkled (from noz-zles) onto the base. A bright industrial fluxing agent was then applied on top of the glaze. In the ropework pieces, both the braided shape (achieved using plaster moulds) and the copper sheen technique (using a quartz-rich copper glaze) were reproduced. The pieces were single-fired at temperatures of 980–1000 °C, the white tiles in an electric kiln and the braided rope pieces in a gas-fire kiln.

In this research a comparative study of the glazed ceramic pieces -original and replacement- from the Madrilenian Chamberí Metro Station was carried out using a multidisciplinary approach. The aim was to find out more about the materials and technologies used to make these pieces, a very characteristic decorative feature of the architecture of Madrid at a very specific time in history, the early 20th century. With this in mind, documentary sources and professional ceramic makers were consulted. The Chamberí Metro station, which in 2019 celebrates its first centenary, is unique in that it is the only station in Madrid that has been conserved almost intact in its original state.

2. Materials and analytical techniques

2.1. Samples studied

The tiles that covered the original walls and ceilings were mainly white bevelled rectangular tiles made in Onda (Figs. 1b–e). These tiles were not studied as no samples were provided. Curved white tiles (also made in Onda) were used in some of the joints between the different planes (CT_O tiles) (Fig. 1b). As well as making the station brighter and easier to clean, the fact that such a large number of white tiles had to be produced led the manufacturers to economize as far as possible in the production process. The passenger information panels were framed in

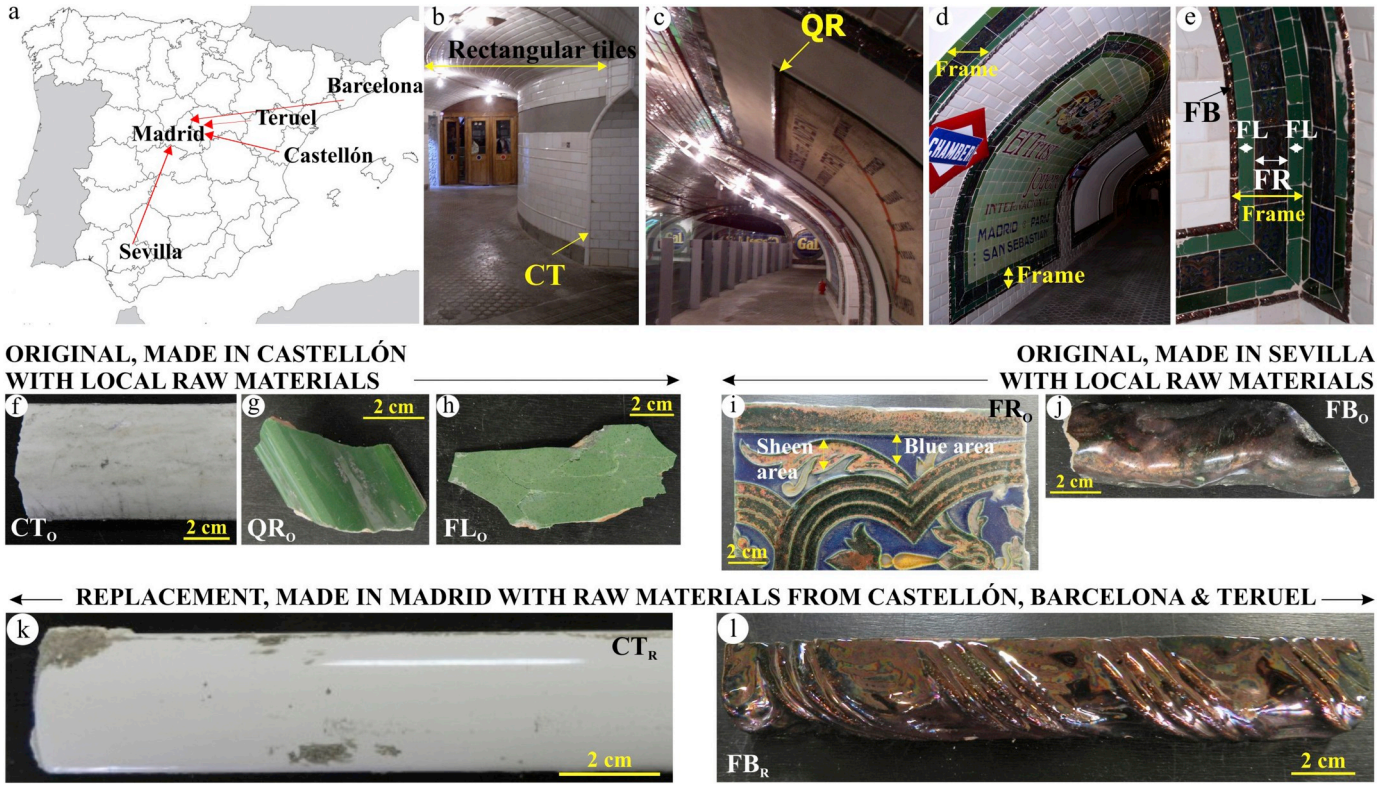

Fig. 1. Glazed ceramics from the Chamberí Metro Station in Madrid, Spain.
a. Spanish provinces that sourced the raw materials used to make the ceramic bodies.
b–e. View of the station in 2008, after the cleaning, conservation and restoration works.
f–l. Samples of the glazed ceramics studied.

Table 1
Typologies of the glazed ceramics and the analytical techniques.

		XRF	XRD	POM	SEM-EDS
		Bases	Bases	Bases & glazes	Bases & glazes
Curved tiles (white)	Original (CT_O)	X	X	X	X
	Replacement (CT_R)	X	X	X	X
Quarter-rounded moulding (green)	Original (QR_O)	X	X	X	X
Framing					
Relief-tiles with metallic sheen	Original (FR_O)	X	X	X	X
Listello tiles (green)	Original (FL_O)	–	X	X	X
Braided rope with metallic sheen	Original (FB_O)	X	X	X	X
	Replacement (FB_R)	X	X	X	X

green quarter-round moulding (QR_O pieces) (Fig. 1c), which may also have been made in Onda. On the platform, the advertising panels and some of the joints between different planes were decorated by a frame formed by (Fig. 1d and e): i) blue relief-tiles with decorative motifs in copper sheen (FR_O tiles), by the Seville ceramic makers Mensaque Ro-dríguez, ii) green, rectangular listello tiles (FL_O tiles) -possibly made in Onda- bordering the relief-tile, and iii) long narrow tiles with a braided rope pattern and a copper sheen (FB_O pieces), made at the Seville ceramic factory of Manuel Ramos Rejano (Perla, 2001). The glazed ceramics used at the station can be divided into two groups on the basis of their specific function: i) pieces of an essentially practical or func-tional nature, with no surface decoration (CT_O, QR_O, FL_O and CT_R) and

ii) pieces of a clearly decorative nature with a metallic sheen and de-corated surfaces (FR_O, FB_O and FB_R).

To the naked eye, the glazes used on the original CT_O tiles have a white hue (Fig. 1f), and those on QR_O and FL_O are green (Fig. 1g and h). The surfaces of the QR_O pieces have an intense, uniform brightness. The compositional motifs in the FR_O tiles have a metallic sheen while the rest of the piece is dark blue (Fig. 1i). FB_O pieces have a partially worn, copper sheen and the overly smooth surface of the braided motif sug-gests that worn-out moulds were used (Fig. 1j). The very bright white tone of the glaze on HC_R (Fig. 1k) is due to the industrial fluxing agent applied on the surface. The FB_R pieces have a very bright, copper sheen (Fig. 1l).

2.2. Analytical techniques

The ceramic bases and the glazes on both the original (CT_O, QR_O, FR_O, FL_O and FB_O) and the replacement (CT_R and FB_R) pieces were analysed in a combined multi-analytical study using: i) X-Ray Fluorescence (XRF), ii) X-Ray Diffraction (XRD), iii) Polarizing Optical Microscopy (POM) and iv) Scanning Electron Microscopy with Microanalysis of Energy Dispersive X-Ray Spectroscopy (SEM-EDS)(Table 1).

X-Ray Fluorescence (XRF) was used to perform chemical analyses on the bases. A Philips Magix Pro PW-2440 wavelength dispersive

sequential spectrometer with a 4 kV X-ray generator was used to ana-lyse the major elements. The accuracy of the analytical results was evaluated by comparing them with certified values for reference ma-terials analysed in previous research (Govindaraju, 1994). Typical ac-curacy is higher than 1.5% relative to a concentration of 10%. Loss on ignition was determined gravimetrically as the weight loss was re-corded between 110 °C and 1000 °C. The De Jongh model (De Jongh, 1973) was followed to convert the intensities into concentrations using Alpha-coefficients. The bases of the FL_O tiles were not analysed using this technique because an insufficient amount of sample was provided.

Mineralogical analysis of the ceramic bases was performed using (XRD). The measurements were taken between 2 and 68°2θ, with an interval of 2°/min in continuous mode, on the total sample. A PHILIPS ANALYTICAL PW 1752 diffractometer operating at 40 kV and 30 mA, with a copper anode tube and a graphite monochromator, was used. The mineral phases were identified using the PC-ADP DIFFRACTION software.

The ceramic bases were described in a handheld sample and in thin sections that were partially stained with alizarin red (Friedman, 1959). Both the bases and the glazes were observed by Polarizing Optical Microscopy (POM), using the OLYMPUS BX51 microscope with an OLYMPUS DP12 Digital camera coupled.

The microstructure and the chemical element composition of the bases and the glazes were studied by Scanning Electron Microscopy and Microanalysis of Energy Dispersive X-Ray Spectroscopy (SEM-EDS). The JEOL JSM 6400 scanning electron microscope, with an acceleration voltage of 0.2 to 40 kV, a current of 6×10^{-10} A, vacuum conditions of 10^{-5} Torr, a resolution of 35 Å and a working distance of 8 mm and 35 kV, was used. The samples were observed in polished thin sections and coated with graphite in the QUORUM Q150TE carbon coater to make them conducting. The images were acquired in secondary elec-tron modes at an acceleration voltage of 20 kV. Semiquantitative che-mical analyses were performed to calculate the percentage in weight of the chemical elements that make up the main components of the bases and glazes. Three zone analyses were carried out per sample in areas of glaze that were free of particles and/or crystals and the percentages in weight of the corresponding oxides were considered. An Oxford Inca Energy Dispersive X-Ray microanalysis system, with a nominal resolu-tion of 133 eV at 5.39 kV was used.

3. Results and discussion

3.1. Ceramic bodies: Original and replacement pieces

3.1.1. Chemical composition (XRF)

There were significant similarities in the content of the main oxides in the original pieces, CT_O and QR_O on the one hand and FR_O-FB_O in the other (Table 2). These pieces had a very high calcium oxide content (> 16%), extremely high in CT_O and QR_O (22–23%), which explains the significant loss due to calcination (> 6%). The replacement pieces had a significant different composition when compared both with each other and with the originals. CT_R and FB_R have a silica content of over 55%. The highest iron oxide (≈6%) and titanium oxide (1.2%) levels were found in FB_R, which also had a very high aluminium oxide content (≈25%).

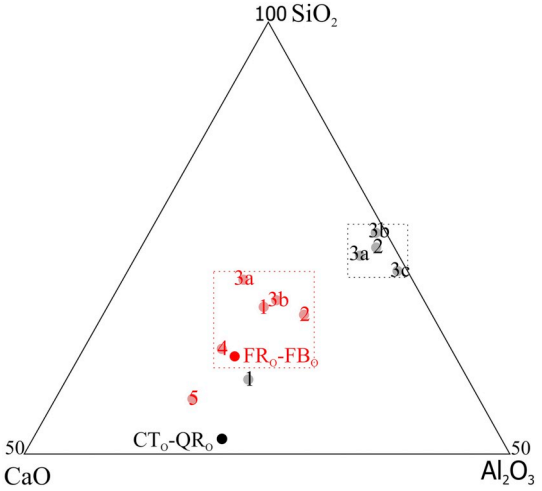

Fig. 2. SiO_2-Al_2O_3-CaO ternary diagram.
The chemical composition of the ceramic bodies of the original pieces and of clayey materials/fired products are represented. From Castellón (in black), from Seville (in red).

The results obtained for the original pieces and the data provided by bibliography are displayed in the SiO_2-Al_2O_3-CaO ternary plot (Fig. 2). The compositions of clayey materials and fired products from different outcrops in the province of Castellón are plotted in black: 1) Miocene clays from Sitjar (Sanfeliu et al., 1989), 2) Fired products from cre-taceous clays (Jordán et al., 1999), 3) Permo-Triassic Moro clays - lower (a), middle (b) and upper (c) Units (Jordán et al., 2009), and from the province of Seville in red: 1) Illitic-calcareous clays (González-García et al., 1988), 2) Mixtures of calcareous and non-calcareous clays (González-García et al., 1990), 3) Industrial bricks -red (a) and yellow (b)- (Flores et al., 1999), 4) Bricks from the Torre del Oro in Seville (Leguey et al., 2001) and 5) Brick from the Reales Alcázares, in Seville (Rincón et al., 2008). If the CT_O and QR_O pieces were made with clays from different outcrops in the province of Castellón (in black), they must also have been mixed with clayey materials that were especially calcareous and poor in silica. The composition data for FR_O and FB_O coincide with the data for clayey materials from the fertile plain alongside the River Guadalquivir near the city of Seville (in red).

3.1.2. Mineralogical composition (XRD)

In CT_O, QR_O, FR_O and FB_O the mineral paragenesis of the ceramic bodies was made up -in order of abundance- of quartz, calcite, gehle-nite, diopside, feldspars *s.l.* and hematites, while the paragenesis of the FL_O tiles was quartz, calcite and feldspars *s.l.* As for the replacement pieces, the main mineral phases in CT_R were quartz and anorthite, with gehlenite, diopside and hematites also being identified. In FB_R the paragenesis was quartz, tridimite, mullite, hematites, feldespars *s.l.* and illite (Fig. 3).

It should be taken into account that the clayey minerals decompose at around 500 °C except for illite, which undergoes dehydroxylation until it disappears at temperatures of over 950 °C (Cultrone et al., 2001). Gehlenite begins to form above 800 °C and its concentration

Table 2
Chemical compositions of ceramic bases (in wt%).

	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	LOI
CT_O	42.8	15.1	5.2	0.05	2.0	23.0	1.1	2.3	0.5	0.13	7.3
QR_o	42.7	15.4	5.2	0.05	2.4	22.0	1.6	3.5	0.5	0.14	6.4
FR_O	47.9	12.0	4.9	0.09	2.9	17.5	1.6	3.3	0.6	0.16	8.3
FB_O	49.3	10.5	4.3	0.08	2.7	16.7	1.7	2.9	0.6	0.15	11.0
CT_R	61.7	14.8	5.1	0.07	2.2	8.3	1.0	3.6	0.7	0.15	1.7
FB_R	56.6	25.1	6.1	0.10	2.4	3.9	0.3	3.4	1.2	0.15	0.5

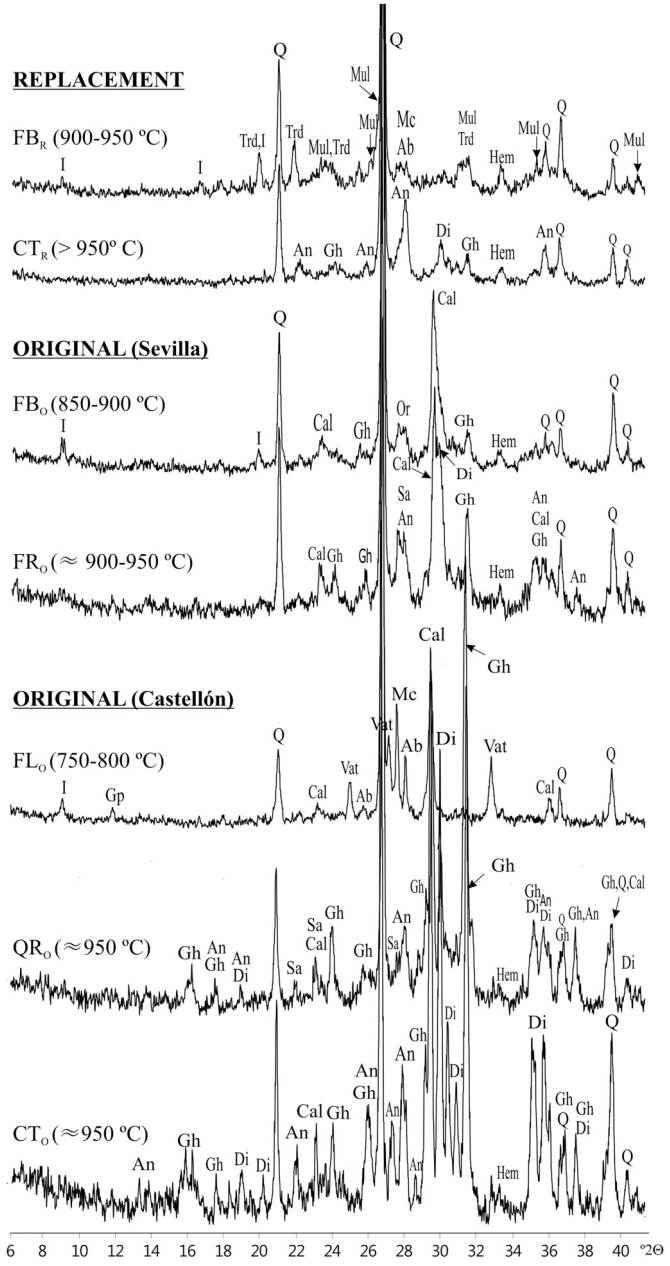

Fig. 3. Mineral paragenesis identified by XRD in the ceramic bodies studied. Albite (Ab), anorthite (An), calcite (Cal), diopside (Di), gehlenite (Gh), hematite (Hem), illite (I), microcline (Mc), mullite (Mul), orthoclase (Or), quartz (Q), sanidine (Sa), tridymite (Trd), vaterite (Vat).

later falls at temperatures of over 1000 °C (Peters and Iberg, 1978). There may be signs of diopside from 800 °C upwards, although its identification using XRD suggests higher firing temperatures of at least 950–1000 °C (Cultrone et al., 2001). The coexistence of gehlenite and diopside indicates firing temperatures of around 950 °C (López-Arce and Garcia-Guinea, 2005). Gehlenite is an intermediate compound which becomes unstable in the presence of silica and with an increase in temperature, reacting to generate newly-formed, more siliceous phases such as anorthite (Peters and Iberg, 1978; Traoré et al., 2000; Cultrone et al., 2001; Trindade et al., 2009). Anorthite begins to form above 900 °C. This temperature is higher in ceramic bodies made with cal-careous clays (Peters and Iberg, 1978; Cultrone et al., 2001, 2004). The presence of high-temperature mineral phases such as wollastonite, gehlenite, diopside and anorthite (≈800–1000 °C) indicates the use of clays that are rich in calcium and/or magnesium carbonate (Peters and Iberg, 1978; Cultrone et al., 2004; Trindade et al., 2009). From 700 ° C upwards in oxidising conditions, small iron oxide particles develop, above all hematites (Maniatis et al., 1981), which have a significant presence as a well-crystallised mineral phase from 900 ° C (Trindade et al., 2009).

These analyses of the mineral paragenesis determined: the coex-istence of diopside and gehlenite in the CT$_O$ and QR$_O$ as well as the presence of anorthite suggested that these pieces were fired at tem-peratures of around 950 °C. Both the presence of calcite and illite and the absence of gehlenite in the FL$_O$ tiles suggested that a maximum temperature of 750–800 °C was reached. The presence of vaterite may be related with microbial activity as it can also be of organic origin (Rodriguez-Navarro et al., 2007). Gypsum was also identified. Its pre-sence may be due to the sulphatation processes that affect the pieces in situ. In FR$_O$, the intensity of the reflections characteristic of the an-orthite, diopside and gehlenite phases suggested that the tiles were fired at temperatures of between 900 and 950 °C. The FB$_O$ pieces appeared to have a firing temperature of around 850–900 °C, as dehydroxylated il-lite was found together with gehlenite and diopside. Calcite was iden-tified in most of the original pieces, together with the newly-formed calcium silicates (gehlenite, diopside and anorthite). Given that car-bonates and high-temperature silicates cannot appear together (Fabbri et al., 2014), it seems likely that calcite comes from the mortars used in the tiling of the walls and it has precipitated as a secondary calcite (López-Arce and Garcia-Guinea, 2005). As regards the replacement pieces, the significant presence of anorthite in CT$_R$, together with the joint presence of diopside and gehlenite, indicated on the one hand that a temperature of over 950 °C must have been reached during firing, and also that a clayey mix made up of illite-kaolinite clays and calcite must have been used. It also pointed out that the recrystallisation reaction according to the metakaolinite-gehlenite-anorthite sequence must have taken place during the firing process, enhanced to a large extent by the structural similarity between the three mineral phases (Traoré et al., 2003). Kaolinite decomposes to amorphous metakaolinite at 500 °C due to the removal of the hydroxyl groups from the silicate lattice (Chen et al., 2000; Toledo et al., 2004). Gehlenite is generated by the reaction between the metakaolinite and the calcium (Traoré et al., 2000) and when the gehlenite reacts with the alumina and the silica from the metakaolinite, anorthite is formed.

Kaolinite → Metakaolinite

$$Al_2Si_2O_5(OH)_4 \rightarrow Al_2Si_2O_7 + 2H_2O$$

(Kaolinite descomposition to metakaolinite at 500ºC)

Metakaolinite + (2 + n)CaO → Gehlenite

$$Al_2Si_2O_7 + (2+n)CaO \rightarrow Ca_2Al_2SiO_7 + nCaOSiO_2$$

Gehlenite + 3SiO$_2$ + Al$_2$O$_3$ → Anorthite

$$Ca_2Al_2SiO_7 + 3SiO_2 + Al_2O_3 \rightarrow 2CaAl_2Si_2O_8$$

The presence of mullite in the FB$_R$ pieces pointed to the use of illite-kaolinite clays (Aras, 2004; Wattanasiriwech et al., 2009). The dehy-droxylation of muscovite at about 900 °C favours the nucleation and growth of mullite (Rodriguez-Navarro et al., 2003), whose formation is due mainly to high aluminium content (Khalfaoui and Hajjaji, 2009). Kaolinite is transformed into mullite and cristobalite through various reactions that result in metakaolinite, a spinel-type microcrystalline phase (or gamma alumina with silicon) and amorphous silica (Sonuparlak et al., 1987; Lee et al., 1999; Chen et al., 2000). El Ouahabi et al. (2015) highlighted that tridymite may be produced as an inter-mediate phase prior to the formation of the cristobalite:

Although mullite appears at around 1100 °C, during the firing of clays with a highly varied composition it can be formed at about 900 ° C. This is due to the epitaxial growth of mullite after the dehydroxylation of the muscovite, which minimizes the energy necessary for its nu-cleation, and the liberation of water after the decomposition of the muscovite (Rodriguez-Navarro et al., 2003). The mineral paragenesis identified in the FB$_R$ pieces -quartz, tridymite, mullite, haematites and

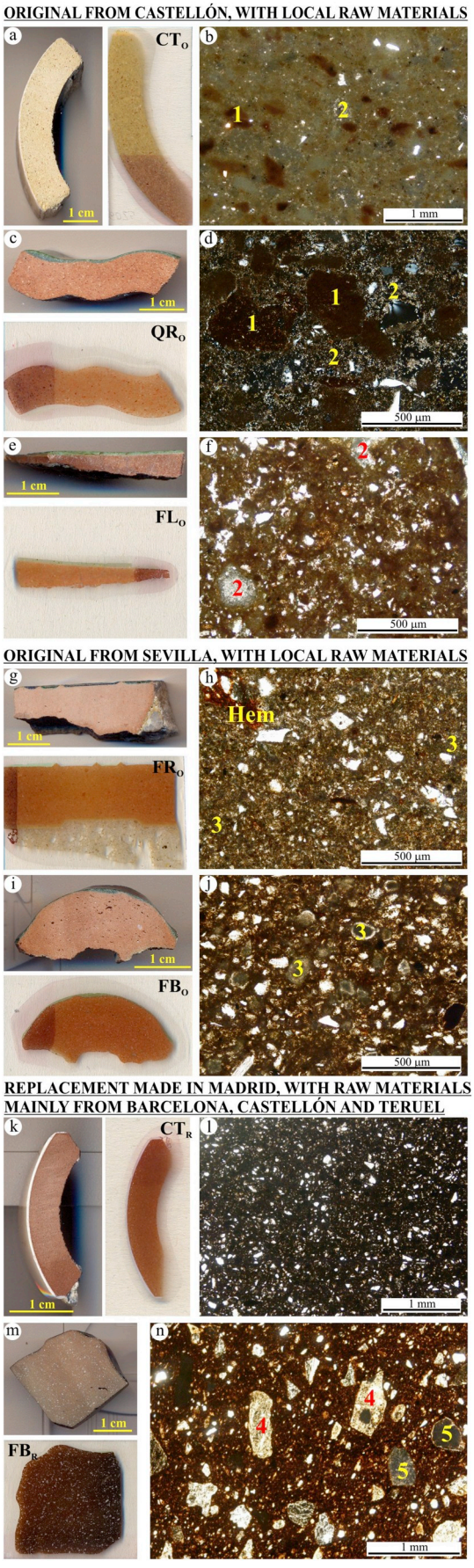

Fig. 4. Ceramic bodies: as seen by the naked eye, thin sections and POM images. PL: plane light (f, h, j, l, n), CL: cross light (b, d). Iron oxides-oxy-hydroxides (1), secondary calcite (2), primary carbonates (3), highly altered inclusions (4), inclusions with amorphous texture (5) and hematite (Hem). illite- therefore suggested a firing temperature of between 900 and 950 °C.

$T \approx 980\ ^{o}C$,

$$\underset{\text{Metakaolinite}}{2SiO_2 \cdot Al_2O_3} \rightarrow \underset{\gamma\text{-alumina}}{Al_2O_3} + \underset{\text{Amorphous}}{2SiO_2}$$

$T > 1100\ ^{o}C$,

$$\underset{\gamma\text{-alumina}}{Al_2O_3} + \underset{\text{Amorphous}}{2SiO_2} \rightarrow \underset{\text{Mullite}}{1/3(3Al_2O_3 \cdot 2SiO_2)} + \underset{\text{Amorphous}}{4/3SiO_2}$$

$T > 1200\ ^{o}C$,

$$\underset{\text{Mullite}}{3Al_2O_3 \cdot 2SiO_2} + \underset{\text{Amorphous}}{4SiO_2} \rightarrow \underset{\text{Mullite}}{3Al_2O_3 \cdot 2SiO_2} + \underset{\text{Cristobalite}}{4SiO_2}$$

3.1.3. *Macroscopic and petrographic description (POM)*

To the naked eye, large numbers of dark-coloured lumps were visible on the CT_O and QR_O pieces (Fig. 4a and c) and FL_O shows a degree of cracking (Fig. 4e). FB_O has a groove on the bottom (Fig. 4i) left by the convex mould on which the pieces were placed inside the kiln to ensure that their shape remained unaltered during firing. When these long, narrow pieces were fixed to the wall, this groove fitted into a tongue jutting out of the wall (tongue and groove). In the FB_R pieces the amount of inclusions is especially significant, some of which have a glassy appearance and a milky tone (Fig. 4m).

Under POM, the CT_O-QR_O-FL_O pieces had an irregular texture -with numerous areas rich in iron oxides and/or hydroxides- and the precipitation of secondary calcite partially filling the pores (Fig. 4b, d and f). This was most significant in FL_O as the ceramic body proved more porous. There was significant presence of quartz-rich inclusions, whose angular morphology, mosaic texture and undulose extinction suggested that they were of metamorphic origin.

Grains of quartz were observed in the FR_O-FB_O pieces and areas with large amounts of iron oxides/hydroxides were more frequent than in the CT_O-QR_O-FL_O. On occasions they had a more crystalline appearance, possibly due to hematites crystallization (Fig. 4h). They show primary carbonates, which in FB_O have been altered at the edges (Fig. 4j). In FB_O, phyllosilicates are also observed.

As regards the replacement pieces, the CT_R tiles had very abundant inclusions of quartz and the matrix had a very homogeneous dark brown colour (Fig. 4l). In FB_R the matrix had a reddish tone and a significant presence of inclusions (Fig. 4n) in the form of monocrystalline quartz, and other larger inclusions of two main types. Firstly, rounded inclusions with a greyish hue, partially amorphous texture and a grain size of over 300 µm, and secondly, prism-shaped and/or subrounded inclusions with grain sizes of up to 800 µm and a high degree of alteration. The distinctive texture of the first type and the intense alteration observed in the second suggest that these inclusions were affected to a greater or lesser degree during firing.

3.1.4. *Microstructure and chemical composition (SEM-EDS)*

The high calcium content detected (≈24%) in the CT_O tiles is largely due to the presence of gehlenite, anorthite, diopside. The reaction interphase around the quartz inclusions (Fig. 5a) is the result of the formation of these phases during firing. The microstructure of QR_O, FR_O and FB_O -vitrification with the formation of fine pores, deformed phyllosilicates, partially grouped together and joined by sintering bridges (Fig. 5b, d and e)- suggests firing temperatures of 850–950 °C (Cultrone et al., 2004). In FL_O (Fig. 5c) there are no signs that temperatures of over 800 °C were reached during firing and a very high calcium content (≈40%) was observed. This was due above all to the abundant precipitation of secondary calcite (Fig. 4f), although the

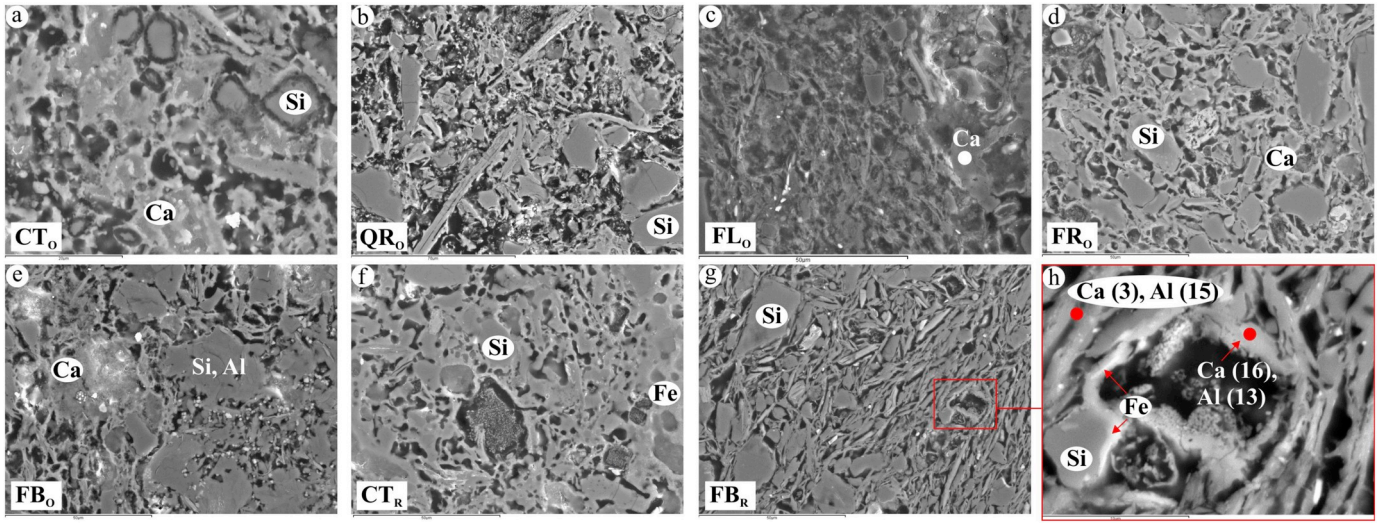

Fig. 5. Characterization using SEM-EDS of the ceramic bases studied.
The microstructure suggests firing temperatures of 850–950 °C (QR_O, FR_O and FB_O), < 800 °C (FL_O), 950–1000 °C (CT_R) and < 850 °C (FB_R). Some of the main elements detected by EDS and the percentage in weight of those identified in FB_R pieces are shown.

presence of primary calcite is not discarded.

The CT_R tiles have the characteristic microstructure of a ceramic material with a high degree of sintering (Fig. 5f), which suggests firing temperatures of between 950 and 1000 °C. The microstructure of FB_R -isolated inclusions and laminar structure of the phyllosilicates (Fig. 5g)- is characteristic of ceramic materials fired at temperatures of up to 850 °C. This observation does not coincide with the data provided by XRD (900–950 °C). The FB_R pieces show abundant inclusions of quartz, iron-rich phyllosilicates (up to 33% iron) and aluminium (≈11%), as well as particles rich in iron (21%) and titanium (20%). Inclusions with either prism-shaped or irregular morphologies were observed, which corresponded to plagioclase with severely altered (due to sericitization) calcium-rich nuclei that had reacted with the silica to form gehlenite on the edges (Fig. 5h). As almost nothing is left in the nuclei and only the edges are preserved, all that remains is the fin-gerprint of these inclusions.

In this case, mullite and tridymite phases identified using XRD do not correspond with the mineral phases generated as a result of firing. This process makes POM identification of the intense sericitization of the plagioclases difficult. The sericitization of the plagioclase favoured the formation of gehlenite during firing, when they reacted with the aluminium-rich clay matrix. This newly-formed phase was limited to the edges of the inclusions, due above all to the minimal calcium oxide content in the clays used to make the FB_R pieces (< 4%) and the low firing temperatures reached (< 850 °C).

The main textural and compositional data for the ceramic bases are set out in Table 3.

The CT_O and QR_O were made using a mixture of clays with varying carbonate content and quartz of metamorphic origin, raw materials typically used by the ceramics industry in Castellón (Sanfeliu et al., 1989; Sanfeliú, 1991; Jordán et al., 1999, 2009). The newly-formed mineral phases identified, their abundance and the extraordinarily high percentage of calcium oxide all suggest that especially calcareous clays were used or even that the manufacturers were deliberately trying to ensure the addition of carbonates. Given that the purpose of the CT_O tiles was to make the spaces used by Metro passengers brighter, it was logical to select clayey materials that were very rich in carbonates, as the calcite phases generated during firing trap the iron -the main cause of the darkening of ceramic bodies- within their structure (Maniatis et al., 1981), so preventing it from spreading throughout the body. In addition, the use of light-coloured ceramic bodies would ensure op-timum use of the white hue provided by the opaque glaze. Besides, calcareous clays begin to melt at lower temperatures (around 800 °C) than clays that are poor in carbonates (Tite and Maniatis, 1975), due to the presence of calcium and magnesium fluxes (Segnit and Anderson, 1972). Given the huge number of CT_O tiles to be produced, the selection of calcareous clays would seem to have been a deliberate decision as a means of reducing production costs as far as possible. The petrographic characters observed in the FL_O tiles suggest that they may also have been made in Onda with a very similar clayey raw material to that used to make the CT_O and QR_O pieces. However, their mineralogical com-position points to low firing temperatures that did not allow the for-mation of high-temperature phases. The result was more porous bases.

With regard to the ceramic bodies of the pieces made in Seville (type FR_O and FB_O), their similar chemical, mineralogical and textural com-position suggests that they were made out of clayey materials (specifically, calcareous illite clays) from the same source. Possibly, the calcium carbonate-rich clayey earths found on the plain bordering the River Guadalquivir. The fact that different firing temperatures were reached is probably because they were manufactured in different factories. The FR_O tiles were produced by Mensaque Rodríguez (900–950 °C) and the FB_O pieces by Manuel Ramos (850–900 °C).

As regards the replacement pieces, the data obtained from the analyses coincide with the information provided by the manufacturer about the raw materials used to make the SIO-2® brand products. A mixture of illite-kaolinite and calcareous clays was used in the pro-duction of CT_R tiles and the homogeneity of the ceramic bodies suggests a high degree of mechanization in their manufacturing process. Although these tiles must also provide brightness, the data show that neither particularly light nor carbonate-rich clays were selected. The ceramic bodies for the FB_R pieces were made with illite-kaolinite clays that were very rich in aluminium and iron with a significant addition of grog composed of mullite, tridymite and essentially calcic plagioclase.

One of the main objectives in the manufacture of the replacement pieces was to make the ceramic bodies more resistant. In the CT_R tiles, this was done using anorthitic ceramic bodies that were rich in quartz and had firing temperatures of over 950 °C, and in FB_R, using alumi-nium-rich refractory bodies with added grog. These refractory bodies minimize the appearance of cracks and avoid deformation, an im-portant aspect to consider in this case of long, narrow pieces which unlike the corresponding originals had no grooves and were not fixed in place using any kind of supporting tongue. The results suggest that these refractory pastes could be made into resistant pieces without having to apply especially high firing temperatures, given that the

Table 3
Main textural and compositional data for the ceramic bases.

		XRF (%wt, Table 2)				XRD (Fig. 3)											
		SiO_2	Al_2O_3	Fe_2O_3	CaO	Q	Cal	Gh	Di	Fk	Ab	An	Hem	I	Trd	Mul	T (°C)
ORIGINAL PIECES																	
Castellón	CT_O	42.8	15.1	5.2	23.0	> + +	+ + +	+ + +	+ + +	−	−	+ + +	+	−	−	−	≈950
	QR_O	42.7	15.4	5.2	22.0	> + +	+ + +	+ + +	+ +	+	−	+ +	+	−	−	−	≈950
	FL_O	−	−	−	−	> + +	+ +	−	−	+ +	+ +	−	−	+	−	−	750–800
	CT_O-QR_O-FL_O: mixture of clays -especially calcareous- with varying carbonate content and quartz																
Seville	FR_O	47.9	12.0	4.9	17.5	> + +	+ +	+ +	+ +	+	−	+ +	+	−	−	−	900–950
	FB_O	49.3	10.5	4.3	16.7	> + +	+ +	+	+	+	−	−	+	+ +	−	−	850–900
	FR_O-FB_O: calcareous illite clays																
REPLACEMENT PIECES																	
Barcelona & Castellón	CT_R	61.7	14.8	5.1	8.3	> + +	−	+	+	−	−	+ + +	+	−	−	−	> 950
	Illite-kaolinite and calcareous clays																
Teruel	FB_R	56.6	25.1	6.1	3.9	> + +	−	−	−	+	+	−	+	+ +	+ +	+ +	900–950
	Illite-kaolinite clays very rich in Al and Fe with a significant addition of grog composed of Mul, Trd and An																

		Naked eye		POM (Fig. 4)	SEM-EDS (Fig. 5)
		Colour	Stain	Main petrological features	Main textural and compositional features
ORIGINAL PIECES					
Castellón	CT_O	Yellow	Yes	Irregular texture	Newly-formed phases Ca-rich (≈24%)
	QR_O	Orange	Yes	Iron oxides/hydroxides	Fired between 850 and 950 °C
	FL_O	Orange	Yes	Secondary calcite, quartz-rich inclusions	No > 800 °C, Ca (≈40%)
Seville	FR_O	Orange	Yes	Irregular texture, primary carbonates	Firing temperatures 850–950 °C
	FB_O	Orange	Yes	Iron oxides/hydroxides, phyllosilicates	Firing temperatures 850–950 °C
REPLACEMENT PIECES					
Barcelona & Castellón	CT_R	Dark brown	No	Homogeneous texture Abundant inclusions	High degree of sintering (950–1000 °C)
Teruel	FB_R	Very dark brown	No	Abundant inclusions (high degree of alteration and amorphous texture)	T^a < 850 °C; Fe (33%), Al (11%) Si-rich inclusions, intense seritization plagioclase

mineral paragenesis identified using XRD reveals firing temperatures (900–950 °C) that do not coincide with the microstructure observed using SEM (> 850 °C). More research is therefore required into this kind of pieces.

3.2. Glazes: original and replacement pieces

3.2.1. Petrographic description (POM)

When studied under POM, the opaqueness and flowing texture of the glaze on CT_O and FL_O (Fig. 6a and c) suggests that they were applied with a paintbrush. The glaze in QR_O appears to have been applied in two layers (Fig. 6b). Fragments of glass (Quinn, 2007) and numerous particles (either dark or with an ochre hue) were identified. The uni-formity of the colour and the intense brightness of the glaze in these QR_O pieces (Fig. 1g) may be related to the high concentration of par-ticles in its upper layer.

The relief of glaze on FR_O can be observed (Fig. 6h, also at Fig. 4g). The area with sheen has a strip in which opaque particles accumulate, possibly due to their decantation inside the glaze (Fig. 6e). Grains of quartz were particularly abundant in the areas with sheen, where they were concentrated near the surface of the glaze and reached sizes of up to 200 μm (Fig. 6e and f). At higher zoom, the greenish tone of the glaze in the areas with sheen can be observed (Fig. 6f). This tone is due mainly to the presence of copper. The glaze on FB_O is opaque and has a flowing texture (Fig. 6g and h) which suggests that it was applied with a paintbrush. A green layer was observed in the contact area with the ceramic base (1 in Fig. 6g and h).

The homogenous, compact appearance of the glaze on the CT_R tiles (Fig. 6i and j) is due above all to the fact that it was applied me-chanically. The FB_R pieces have numerous fragments of glass (Fig. 6r) with rounded edges, which are components of the copper glaze. There is a very significant presence of small crystals in the interphase (Fig. 6l).

The glazes applied to the ceramic bases can be observed. All the images were taken with plane light except Fig. 6i, with cross light.

3.2.2. Microstructure and chemical composition (SEM-EDS)

The CT_O-QR_O-FL_O pieces contain bright arsenic-rich (12–19%), calcium (4–7%) and chlorine (2–3%) particles (Fig. 7b, c and e), which are particularly abundant in CT_O (Fig. 7b). Arsenic is used as a fining agent in glazes so as to minimize the appearance of bubbles (Vielhaber, 1954), normally in proportions of < 1%. Its high concentration in these glazes suggest that these are lead-rich arsenate particles, which make the glaze more opaque (Fernández-Navarro, 2003), in the absence of tin oxide. In fact, tin was not detected in any of the analyses carried out on these three kinds of pieces. In QR_O and FL_O, particles with varying proportions of chrome (16% and 40%) and cobalt (2% and 25%) were identified. In QR_O these particles also had a significant zinc content (6%). There are green colourants based on a combination of chrome oxide and cobalt oxide, to which zinc oxide may be added as an in-tensifier of the colour (Lowery and Scabbiolo, 1978). These particles may therefore be responsible for the green colour of the glaze on the QR_O and FL_O pieces. The glaze on the QR_O pieces has grooves in which high aluminium contents (24% and 35%) were detected (Fig. 7c). These may be the result of the porosity produced when the glaze crystallizes. In CT_O and QR_O the contact is continuous and straight, and is parti-cularly straight in QR_O (Fig. 7c). There is almost no interphase, with very few small crystals being identified (1 in Fig. 7a and c). In FL_O there is a high degree of interpenetration between the glaze and the body (Fig. 7d).

The interphase of the FR_O tiles shows the formation of abundant, small, needle-shaped crystals (Fig. 7e and f) made up above all of si-licon (24%), lead (8%), calcium (8%), aluminium (7%), and potassium (4%). As well as corresponding above all to lead feldspars, the sub-stantial calcium content detected in these crystals (≈8%) together with the high percentage of CaO in the bases (Table 2) suggest that they may also be calcic pyroxenes whose formation has been detected in inter-phases with ceramic bodies made with calcareous clays (Molera et al., 2001). Near the surface of the area with sheen there are grains made up exclusively of silicon, which are over 100 μm in size. Around these

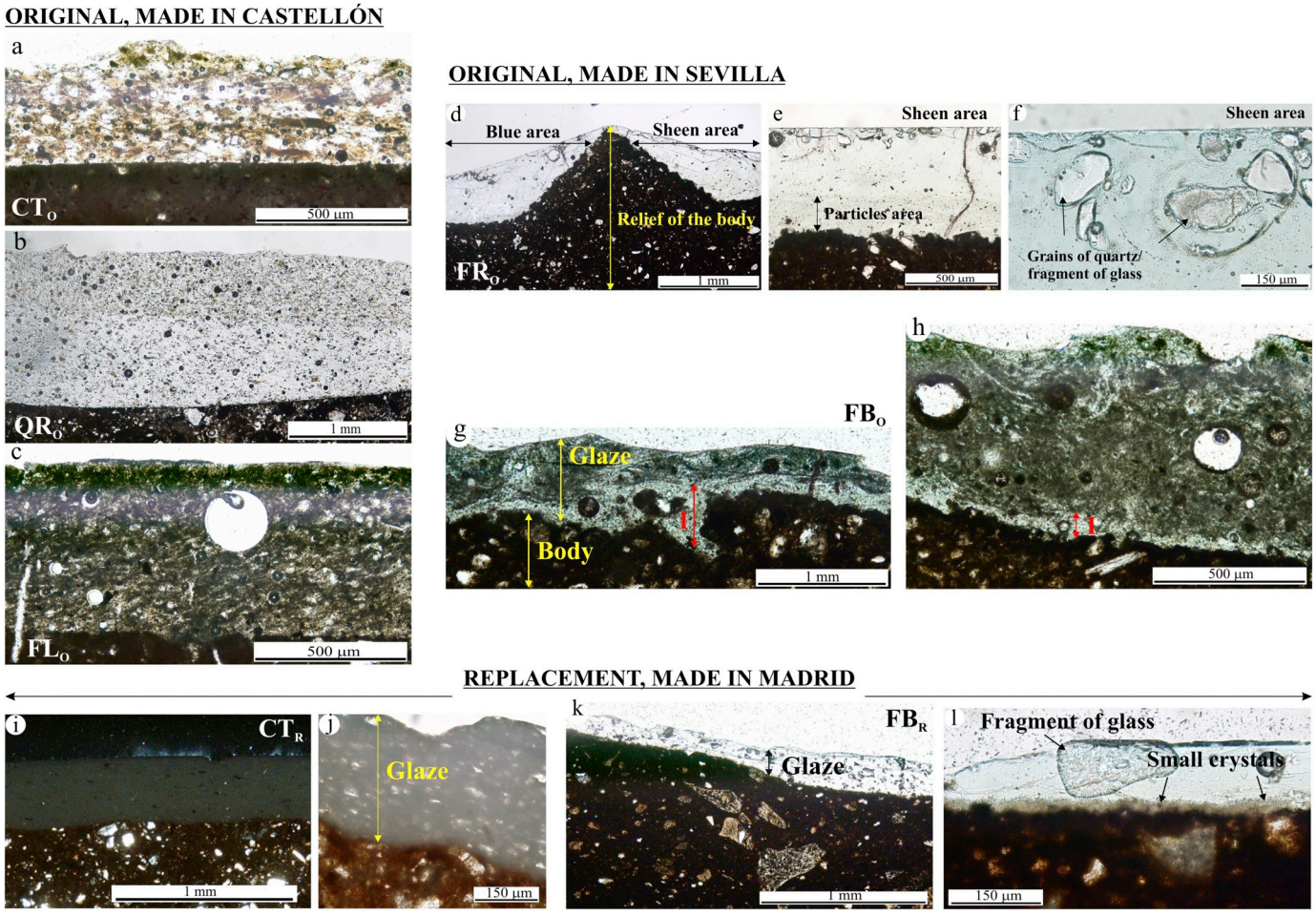

Fig. 6. Polarized Optical Microscopy images (bases and glazes).

grains, there are abundant fissures where a high tin content (28%) has been identified (Fig. 7e). The material found in the interphase in the FB_O pieces (Fig. 7g) has a similar texture to the ceramic body and a varying thickness. Made up above all of silicon (21%), calcium (10%) and aluminium (10%), this is the light green layer observed previously with POM (1 at Fig. 6g and h). In some cases, crystallites form in the contact between this layer and the glaze (1 in Fig. 7g). However, in those areas in which this material is not in contact with the glaze, a very dark layer (or pore) shaped like a curved line can be identified. Various areas can be identified in the glaze: i) above this layer or pore, an area with abundant bright particles rich in tin (44%) and lead (12%) and greyish particles with calcium (6%), iron (3%), copper (4%) and lead (20%) (Fig. 7h), ii) an area with feldspars with hardly any bright par-ticles, and iii) another area which also has abundant bright particles (Fig. 7g) rich either in tin (60%) or in lead (46%) and copper (4%).

In CT_R tiles, bright polygonal crystals that were very rich in zircon (42%) and also contained iron (5%) were identified. These crystals were especially numerous in the diffuse contact area with the base, and were also trapped in its pores (Fig. 7i). The glaze also contains abundant smaller feather-shaped crystals with dendritic growth (Fig. 7j) made up essentially of silicon (21%) and zirconium (5%). These are zirconia (ZrO_2) crystals. In FB_R, large numbers of grooves with high aluminium contents (27% and 33%) were also identified. The interphase is quite thick (40–60 µm) and the formation of abundant, small needle-shaped crystals (Fig. 7k and l) made up above all of silicon (21%), lead (15%) and aluminium (10%) was observed. These crystals are aluminium lead feldspars whose formation was favoured by the high aluminium content in the glaze and the bases, made with highly aluminous clays (Table 2).

All the images are of transversal sections. The main features of the interphases and the particles and/or crystals identified on the glazes can be observed.

Semiquantitative analyses were carried out on the glazes using EDS in areas with no particles and/or crystals (Table 4). The glazes from the original pieces in both CT_O-QR_O-FL_O and FR_O-FB_O are essentially lead-alkaline with alumina. The glaze on the CT_R tiles is a silicon-alkaline glaze with zirconium oxide and significant alumina, calcium oxide and alkali contents, FB_R has a lead-potassium glaze (free of sodium oxide) with a high alumina content.

The correlation diagrams display the similar composition of the original glazes according to the group of pieces to which they belong (Fig. 8). Tite et al. (1998) pointed out that lead glazes were first used in the Western world around the first century BCE. These were transparent glazes with a high lead content (45–60%), an alkaline content of < 2%and an aluminium content of between 2 and 7%. They also stated that lead alkali glazes began to be used in the 10th and 11th centuries and had a 20% to 40% lead oxide content and were 5% to 12% alkalis. On this basis and in view of their lead oxide and alkali contents (Fig. 8a), the glazes on CT_O-QR_O-FL_O can be classified as lead alkali glazes (≈35% PbO and ≈6% alkalis). Those on the FR_O and FB_O pieces are mainly transparent high lead glazes (≈48% PbO, ≈3–4% alkalis and ≈1.7% Al_2O_3), although their alkali content is slightly higher and the proportion of alumina is slightly lower than in the transparent high lead glazes referred to by Tite et al. (1998).

Considering the ratio between oxides that form and oxides that modify the glaze network (Fig. 8b), the same grouping of glazes for the original pieces were obtained, with the glazes on QR_O and CT_O proving especially similar. The CT_R glaze is totally different from all the others,

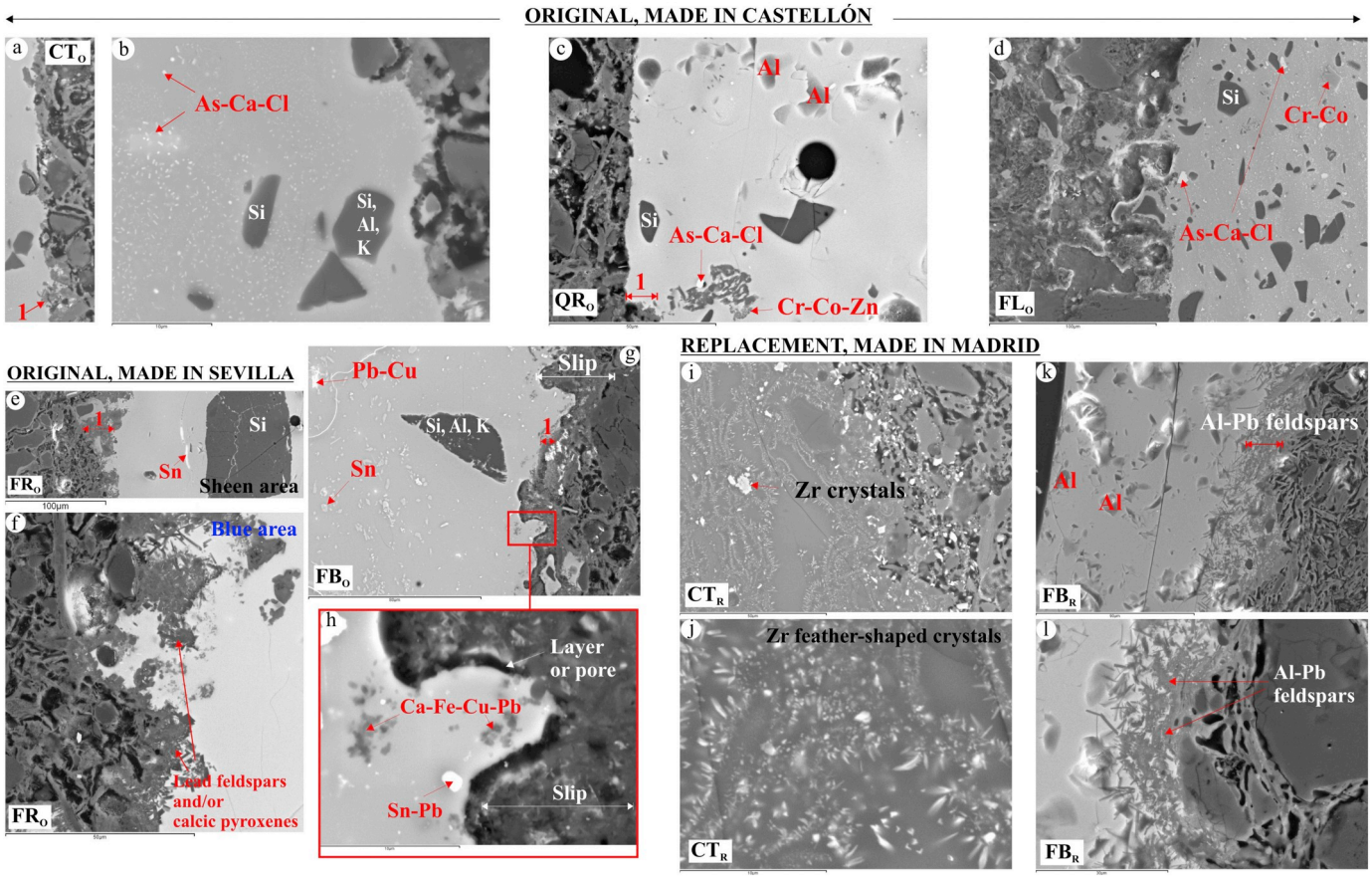

Fig. 7. SEM-EDS characterization of the glazes.

Table 4
Chemical compositions of glazes (in wt%).

	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	CuO	ZrO_2	PbO
CT_O	2.2	0.0	4.0	54.7	2.8	0.0	0.0	0.0	0.0	36.3
QR_o	1.7	0.0	3.5	54.2	4.2	0.0	0.0	0.0	0.0	36.4
FL_O	2.4	0.0	4.4	57.4	5.1	0.0	0.0	0.0	0.0	30.8
FR_O	1.9	0.0	1.9	45.3	2.5	2.1	0.0	0.0	0.0	46.3
FB_O	2.2	0.0	1.5	38.3	0.8	1.9	1.7	4.3	0.0	49.3
CT_R	3.7	2.9	6.8	62.3	3.8	8.9	0.0	0.0	11.6	0.0
FB_R	0.0	0.0	7.4	44.4	1.6	3.8	1.6	4.4	0.0	36.8

in that it is a silicon alkaline glaze and the composition of the glaze on the FB_R falls somewhere between the two groups established for the original pieces. From Geller and Bunting (1936) it is deduced that, for the original glazes and for FB_R, the K_2O, PbO and SiO_2 contents indicate melting temperatures of between 700 and 820 °C.

The general data about the texture and composition of the studied glazes are set out in Table 5.

The original glazes (and FB_R) were fired at low temperatures (700–820 °C), mainly due to the strong fluxing properties of K_2O and Na_2O. These glazes proved very successful because at low temperatures they can produce the fluidity required to cover the ceramic bases properly. The glazes on the CT_O-QR_O-FL_O pieces can be classified as lead-alkali glazes (≈35% PbO and ≈6% alkalis) and their opaqueness

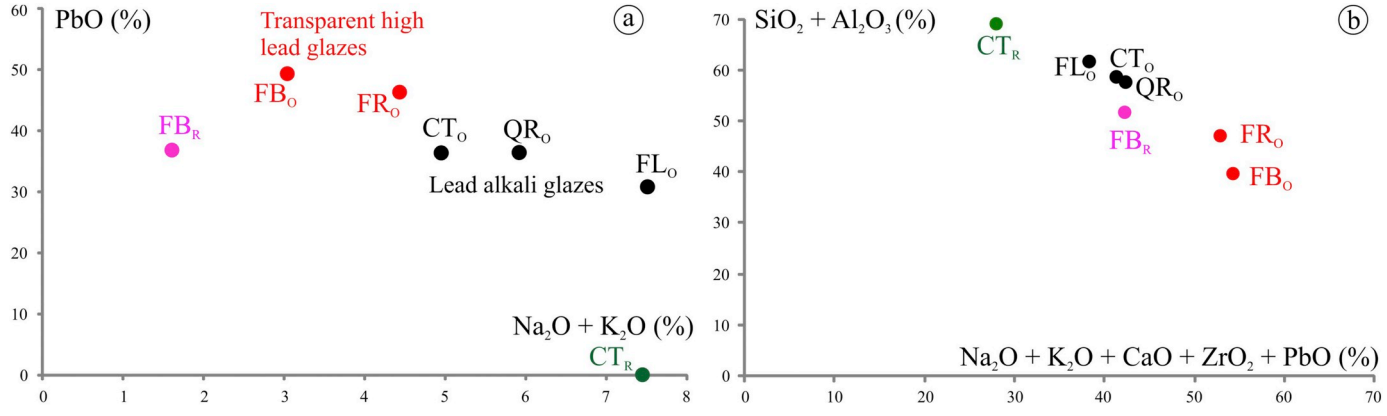

Fig. 8. Correlation diagrams of lead oxide versus alkalis (a) and oxides that form the glaze network against oxides that modify it (b).
The compositional similarity between glazes CT_O-QR_O-FL_O and FR_O-FB_O glazes can be observed. The CT_R glaze has a markedly different composition.

Table 5
Main textural and compositional data for the glazes.

	Naked eye and POM (Fig. 6)					SEM-EDS (Fig. 5)		Body-glaze interphase
	Colour	Texture	Thickness	Particles	Body-glaze contact	Composition		
						Glaze (wt%)	Particles	
ORIGINAL PIECES, made in Castellón								
CT_O	White	Opaque Flowing	Regular, ≈400 μm	Q grains	Continuous Straight	SiO_2 ≈ 55 PbO ≈ 36 Alkali ≈ 5	Q, Feld. Pb-As	Continuous Irregular Crystals (+)
QR_O	Green	Transparent Greenish	Irregular, up to 1 mm 2 layers	Dark and Ochre hue Frag. glass	Continuous Very straight	SiO_2 ≈ 54 PbO ≈ 36 Alkali ≈ 6	Q, Feld. Pb−As Cr-Co-Zn	Continuous Very straight Crystals (+)
FL_O	Green	Opaque Flowing	Regular, ≈600 μm	Q grains	Continuous Irregular	SiO_2 ≈ 57 PbO ≈ 31 Alkali ≈ 8	Many Q, Feld. Pb−As Cr-Co	Continuous Interpenetration
ORIGINAL PIECES, made in Seville								
FR_O	Metallic sheen	Transparent	600 μm, thin towards relief line	Opaque Q grains up to 200 μm	Irregular Some crystals	SiO_2 ≈ 45 PbO ≈ 46 Alkali ≈ 4	Sn Si grains	Irregular Crystals (++)
	Blue	Transparent		Dark	Irregular Some crystals	SiO_2 ≈ 45 PbO ≈ 46 Alkali ≈ 4	Co Si grains	Irregular Crystals (++)
FB_O	Metallic sheen	Opaque Flowing Green	Irregular, 300–700 μm	X	Irregular Slip	SiO_2 ≈ 38 PbO ≈ 49 Alkali ≈3	Sn Sn−Cu Feld.	Irregular Silp Crystals (+)
REPLACEMENT PIECES, made in Madrid								
CT_R	White	Compact Homogeneous	Regular, ≈600 μm	X	Gradual Diffuse	SiO_2 ≈ 62 ZrO_2 ≈ 12 Alkali ≈ 8	Zr-Fe, Si−Zr crystals	Gradual
FB_R	Metallic sheen	Transparent Colorless	Regular, ≈300 μm	Frag. glass	Continuous Straight Many crystals	SiO_2 ≈ 44 PbO ≈ 37 Alkali ≈ 2		Continuous Straight Al−Pb feld. (+++)

is largely provided by the presence of lead-rich arsenate particles. In the case of CT_O (white tiles) this aspect would help reduce costs given the high cost of tin oxide and the enormous number of pieces to be pro-duced. The considerable thickness of the glaze in QR_O is worthy of note as is the presence of particles rich in aluminium and zinc, elements that provide stability to the glaze (Fernández-Navarro, 2003) and make it highly resistant. This is why its original colour and brightness have been conserved practically intact. This aspect, together with the quarter-round mould used on this type of piece, would increase pro-duction costs, although this was probably of limited importance given the relatively small number of this type of pieces used in all the stations (frames for the passenger information panels). The body-glaze contact in CT_O and QR_O suggests that the pieces were fired twice, in other words that the glazes were applied to previously fired ceramic bodies. The interpenetration on the FL_O tiles is due above all to the fact that the ceramic base was more porous (fired at low temperatures, 750–800 °C), so allowing the glaze to soak in. In this type of FL_O pieces, the abun-dance of quartz and feldspar grains, residual inclusions that did not react during the melting of the glaze (Özçatal et al., 2014), suggests low melting points of around 700–760 °C, which would match the tem-peratures deduced on the basis of its composition (Geller and Bunting, 1936).

The glazes on the FR_O-FB_O pieces are classified as transparent lead glazes (≈48% PbO, ≈3–4% alkalis and ≈1.7% Al_2O_3). Both contain copper, an element that produces the metallic sheen, and tin which provides opaqueness. The considerable thickness of the interphase (≈50 mm) in the FR_O tiles and the abundant small crystals that have formed there, suggest that the pieces were single fired, i.e. the glazes were applied on raw ceramic bodies. In the areas with sheen, the sig-nificant presence of quite large grains of silica near the surface could be due to the addition of ground opaline to enhance the iridescent effect or metallic appearance (Rincón et al., 2018). The braided design on the FB_O pieces may have required the additional application of slip, so as to ensure that the glaze adhered as well as possible to the body. Given that slip was normally applied to unfired bodies (Capelli and Cabella, 2013), the deformation observed in this layer and its irregular contact with the ceramic body and also with the glaze -with the formation on occasions of crystallites- suggests that these pieces were single fired. In the re-placement pieces both the diffuse body-glaze contact -with the presence of abundant zirconium-rich particles- in CT_R, and the considerable thickness of the interphase in FB_R, with the formation of abundant small crystals, are due above all to the single firing of both kinds of pieces. The white surface of the CT_R tiles is achieved with a silicon aluminium glaze with alkalis enriched in zircon. Its mode of application, com-pactness and considerable thickness make it difficult for the colour of the ceramic base to influence the final colour of the tile, which could explain why the base has a dark tone even though the glaze is white. This glaze is very common today and provides high mechanical re-sistance to impact and abrasion and high resistance to chemical cor-rosion. The reaction at high temperature between zircon ($ZrSiO_4$) and aluminium leads to the dissociation of zircon, forming abundant zir-conia crystallites (ZrO_2) (Moya et al., 1991). Both the presence of im-purities, often found in commercial zircon fine powders, or the delib-erate addition to the composition of the original frit of alkaline and alkaline earth elements in oxide form, reduce the temperature for the dissociation of zircon and the initial melting temperatures (Pena and de Aza, 1984; Moya et al., 1991; Kaiser et al., 2008). The vitreous phase that is formed by the addition of these oxides favours the precipitation of zirconia crystallites (ZrO_2) (Rincón and Romero, 2000). In addition, the dendritic growth observed using SEM is due to an increase in the diffusion of impurities or additives in the vitreous phase (Rincón, 1992) and to the slowing down of the reactions, so permitting the complete dissociation of the zircon used as a raw material (Rendtorff et al., 2012). In the glaze on the FB_R pieces, the important aluminium content makes the glaze highly resistant. The significant formation of lead-rich feldspar arrangements at the interphase suggests considerable firing

and cooling times, so allowing greater diffusion between the body and the glaze (Molera et al., 2001). These crystals are highly developed, which favours the adherence of the glaze to the body, so increasing the already high resistance of these pieces. In the replacement pieces both the diffuse body-glaze contact -with the presence of abundant zirco-nium-rich particles- in the CT_R tiles, and the considerable thickness of the interphase in the FB_R pieces, with the formation of abundant small crystals, are due above all to the single firing of both kinds of pieces.

4. Conclusions

The materials and technologies used to make the glazed ceramics-original and replacement- of the Chamberí Metro Station in Madrid were analysed and identified. The manufacture of such pieces was influenced by their particular function and by the amount of pieces that had to be produced. Original white tiles (CT_O), quarter-rounded moulding pieces (QR_O) and listello tiles (FL_O) were made using a mixture of clays with varying carbonate content and quartz. CT_O and QR_O were produced with very calcareous clays fired at ≈950 °C and both were coated with lead alkali-glazes. Lead-rich arsenate particles may have been added as an opacifying agent. The FL_O tiles were made with a mixture of clays with varying carbonate content and quartz fired at 750–800 °C, so the bases were more porous. The original decorative pieces (FR_O and FB_O) were made from calcareous and illite clays fired at temperatures of between 850 and 950 °C and treated with transparent lead glazes and the metallic sheen. The addition of ground opaline to enhance the metallic appearance of FR_O tiles is suggested and the ap-plication of a slip on FB_O pieces was observed. The materials and techniques used in the manufacture of the replacement pieces made them especially resistant. The white replacement tiles (CT_R) were made out of quartz-rich, illite-kaolinite and calcareous clays fired at tem-peratures of > 950 °C with an alkali-glaze that was very rich in zircon and aluminium. Decorative pieces of replacement tiles (FB_R) were made from illite-kaolinite clays that were very rich in aluminium, with a highly refractory grog addition, and then covered with an aluminium-rich lead-potassium glaze. Although the microstructure observed with SEM suggested that they were fired at < 850 °C, the XRD results in-dicated much higher firing temperatures (900–950 °C). This exceptional feature of the FB_R tiles is due to the fact that the very high temperature phases identified corresponded to the refractory grog added and not to the firing products. The knowledge acquired will be useful for the conservation of these glazed ceramics, on which further research is required.

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